SELENIUM GEOCHEMICAL RELATIONSHIPS OF SOME NORTHERN NEVADA SOILS

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ABSTRACT.—Soil samples, one from each of 10 locations in northern Nevada, were evaluated for redox potential, total and extractable selenium, phosphate, free iron oxide, total and ferrous iron. Mole fractions for extractable selenium species were calculated from redox potentials. Data were used to extrapolate general geochemical relationships for soil selenium at the sample sites. Results obtained from one sample per location allowed only the most general conclusions to be drawn. Soil phosphate levels, which affect the adsorption of selenite species on iron oxide by competing for adsorption sites, were not correlated with levels of extractable selenium in this study. This would suggest that selenium would exist in solution, having been displaced from adsorption sites by phosphorus. Ferrous iron, iron oxides, and redox potential had a combined effect on the level of extractable selenium at all sites. Soils in this study support selenite species that are not readily available to plants and therefore could not support vegetation adequate in Se.

Key words: selenium, soil, redox potential, geochemistry, plant bioavailability.

Selenium (Se) is a significant micronutrient in production agriculture; because of this, knowledge of the Se status of rangelands is important. Distribution of total and extractable Se can vary widely over short geographic distances (Fisher et al. 1990). Because the geology of Nevada is complex, relationships between critical plant Se levels and geological formations are difficult to define. Recently, a review of the Se status of soils, plants, and animals in Nevada reported deficiency problems in western Nevada, variable amounts in northern and central portions of the state, and adequate levels in the southern portion of the state. Selenium accumulator plants grow throughout Nevada on limited seleniferous geological formations (Poole et al. 1989; Fig. 1). The narrow gap between essential and toxic concentrations of Se makes it imperative that processes controlling the distribution of this element be understood (McNeal and Balistrieri 1989).

Uptake of Se by plants is governed by many soil and plant factors including type of plant, soil pH, clay content, and mineralogy. Most important factors determining uptake are form and concentration in the soil. Chemical form is controlled by redox potential parameters (pe + pH; Elrashidi et al. 1989, Mikkelsen et al. 1989). Although Se may exist in four oxidation states, selenate (VI) and selenite (IV) are predominant mobile forms in a soil solution and are available for plant uptake.

Redox potentials are important in soils, and theoretical relationships can be used to predict and interpret metal solubilities (Lindsay and Sadiq 1983). Redox potentials have been used in Nevada to interpret observed sequences of minerals in an alteration zone in Ely, Nevada (Raymahashay and Hollard 1969), interpret hydrogeochemistry of the Red Rock, Nevada, area (Fricke 1983), and evaluate trace-element content of sediment and water in west central Nevada (Rowe et al. 1991). Soil redox potential data are lacking for the state.

The purpose of this study was to investigate soil Se geochemical relationships for 10 Nevada sites using redox potential (pe + pH) and extractable and total Se levels. Phosphate (P), iron (Fe), and iron oxide (Fe_2O_3) levels were also investigated to determine their effect on Se bioavailability for plants growing on the soils.

EXPERIMENTAL PROCEDURE

A soil sample was taken from each of 10 sites: Battle Mountain and Gund Ranch in central Nevada (Eureka and Lander counties); Minden (Douglas County); Reno, Red Rock area north of Reno, Spanish Springs (Washoe

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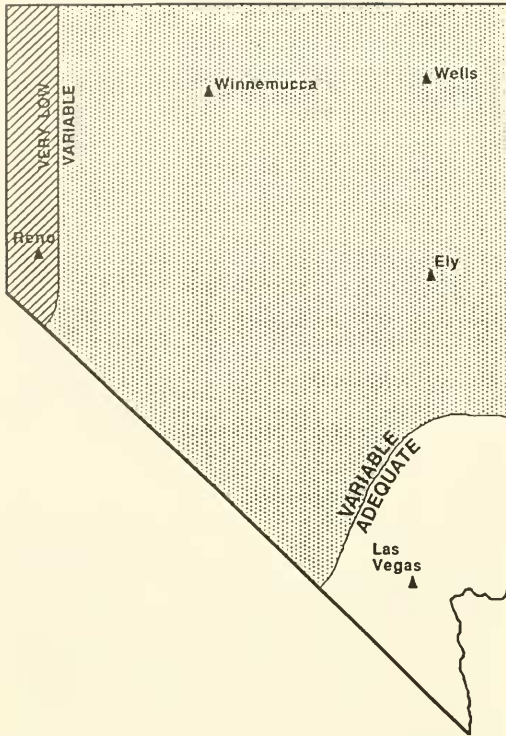
Fig. 1. Selenium in Nevada forage. Very low = 81% of samples with Se concentration of <0.01–0.05 ppm Se; variable = 74% of samples with Se concentration of 0.05–0.5 ppm Se; adequate = 78% of samples with Se concentration of 0.1–1.0 ppm Se.
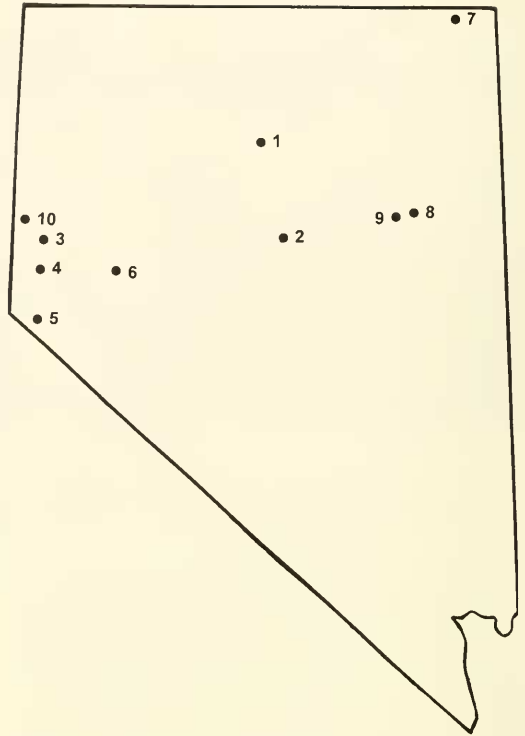
Fig. 2. Soil sample locations in northern Nevada: 1–Battle Mountain, 2–Gund Ranch, 3–Spanish Springs, 4–Reno, 5–Minden, 6–Fallon, 7–Salmon Falls Creek, 8–Huntington Valley, 9–Clover Valley, 10–Red Rock.

County); Fallon (Churchill County); Salmon Falls Creek near Contact and two locations near the Ruby Mountains (Elko County) in Nevada (Fig. 2). Samples were taken approximately 12–15 cm below the surface so as to include the root zone. Air-dried samples <2 mm (No. 10) were used for analysis.

Redox potentials were measured according to the procedure of Lindsay and Sadiq (1983). Soil suspensions were prepared in conical flasks to contain 50 g air-dried soil and 100 mL deionized water. Each treatment was prepared in duplicate, degassed with argon (Ar), stoppered, and shaken. Millivolt readings were taken on soil suspensions with a platinum (Pt) electrode and a glass Ag/AgCl reference electrode using an Altex SelectIon 5000. The platinum/reference electrode system was standardized using a ferrous/ferric ion reference solution (ZoBells; ASTM 1978). Soil suspension pH was determined using a combination electrode that was calibrated with standard buffers (ASTM 1978). Suspension pe was calculated from millivolt readings using the relationship pe = Eh(millivolts)/59.2.

To obtain total soil Se levels, we digested samples in aliquots of 1:1 hydrochloric acid and 5% potassium persulfate for 15 min followed by 3.5% oxalic acid solution for 15 min. The resulting solution was then treated with concentrated hydrochloric acid for 42 min prior to diluting to 100 mL volume with deionized water. Se concentrations of the digests were determined using hydride generation atomic absorption spectroscopy (AAS; Varian SpectrAA 10 with VGA accessory).

Soluble Se was measured in a saturation paste extract from each soil (Jump and Sabey 1989) using hydride generation AAS. The extract Se concentration was used for calculation of Se species. The mole fraction of soluble Se species was calculated employing methods of Elrashidi et al. (1987).

Bicarbonate extractable P was determined using the method of Olsen (Council on Soil Testing and Plant Analysis 1980). To evaluate

Fe_2O_3 levels, we extracted 4 g soil overnight with 4 g sodium dithionite ($Na_2S_2O_4$) and 75 mL deionized water. Suspensions were filtered, brought to volume (Kilmer 1960), and analyzed for Fe by AAS. Total soil Fe was determined by flame AAS on nitric acid digests of soil samples.

Ferrous iron (Fe II) in sample soils was determined colorimetrically. Samples were digested using concentrated sulfuric acid and 30% hydrofluoric acid, neutralized with 4% boric acid, and made to volume with deionized water (Walker and Sherman 1962). To an aliquot of the digest we added 0.001 M bathophenanthroline in 50% ethanol and acetate buffer. Isoamyl alcohol extracted the ferrous-bathophenanthroline complex from the solution. The alcohol layer was drained into a 25-mL volumetric flask, made to volume with 95% ethanol, and the absorption of the solution read on a spectrophotometer (Baush and Lomb Spectronic 710) at a wavelength of 538 nm. Standards and blanks were treated similarly. Ferrous iron standards were derived from a stock solution of ferrous ammonium sulfate.

For the interpretation of data, we used redox and adsorption relationships developed by Howard (1977), Balistrieri and Chao (1987, 1990), and Schwab and Lindsay (1983) for the behavior of Se, Fe, and PO_4 and equilibria described by Elrashidi et al. (1987) for Se in soils.

Regression and multiple regression analyses were performed following methods of Damon and Harvey (1987). Regressions were evaluated for significance at the 95% confidence level.

RESULTS

Total Se, extractable Se, redox parameters, and general site descriptions are presented in Table 1 for sample soils. Mole fractions of the Se species for each sample are presented in Table 2.

Howard (1977) summarized Se geochemistry on an Eh-pH diagram and found that Fe, with which Se is closely associated in both oxidizing and reducing environments, controls Se geochemistry. In aerated soil suspensions the Se (IV) oxyanions $HSeO_3^-$ and SeO_3^{2-} are strongly adsorbed by hydrated surfaces of ferric oxides over the pH range 2–8; above pH =

TABLE 1. Total selenium, extractable selenium, redox potential (pe + pH), and predominant selenium species in soil samples.

| Sample location | Selenium[*] | | pe + pH | Predominant Species |
	Total (mg/kg)	Extractable (µg/kg)		
Battle Mountain[a]	0.62	4	10.0	Selenite
Gund Ranch[b]	0.74	8	11.7	Selenite
Spanish Springs[c]	0.10	102	7.5	Selenite
Reno[c]	0.11	<2	11.1	**
Minden[d]	0.20	50	10.9	Selenite
Fallon[e]	1.2	3	11.1	Selenite
Salmon Creek[f]	0.37	26	8.5	Selenite
Clover[g]	0.13	<2	7.6	**
Huntington[g]	<0.10	<2	9.6	**
Red Rock[h]	0.10	7	11.9	Selenite

[*]Air-dried basis
**Could not be calculated due to lack of measurable selenium in extract.
[a]Stewart and McKee 1977
[b]USDA-SCS 1978, USDA-SEA 1980
[c]USDA-SCS 1983
[d]USDA-SCS 1984
[e]Willden and Speed 1974
[f]Schrader 1934, Tueller 1975
[g]Tueller 1975
[h]USDA-SCS 1983, Fricke 1983

8, adsorption decreases to complete desorption at pH = 11. Selenite shows a strong affinity for Fe_2O_3 surfaces (Balistrieri and Chao 1987), forming stable ferric oxide-selenite ($Fe_2(OH)_4SeO_3$) complexes that cause immobilization of Se. Selenate on the other hand shows a weaker affinity for oxide surfaces, forming compounds that are soluble and, therefore, mobile (Howard 1977, Elrashidi et al. 1987, Presser and Swain 1990) and easily transportable in groundwater and available for plant uptake (Lakin 1961).

Levels of extractable Fe_2O_3 are presented in Table 3. Because adsorption of selenite increases with increasing concentration of Fe_2O_3 due to the greater number of available binding sites (Balistrieri and Chao 1987), it follows that soils at Gund Ranch and Spanish Springs have the potential to adsorb the largest amounts of selenite. The Clover Valley sample would be least likely to adsorb selenite. pH would not have an effect on the ability of Fe_2O_3 to adsorb selenite for all the soils except Clover Valley (pH > 8). Levels of Fe_2O_3 and Fe(II) had a combined effect on the amount of Se extracted from soils ($r = .3196$). Iron oxide and Fe(II) were not affected by redox potential ($r = .0705$).

TABLE 2. Log mole fraction of selenium species[a].

Sample[b]	Species								
	SeO_4	$HSeO_4$	H_2SeO_4	SeO_3	$HSeO_3$	H_2SeO_3	Se^{2-}	HSe	H_2Se
1	−9.2	−14.9	−29.2	−0.15	−0.55	−5.6	−22.9	−15.6	−19.6
2	−5.9	−12.3	−22.6	−0.02	−1.32	−7.0	−33.3	−26.6	−31.1
3	−12.2	−17.9	−24.4	−0.18	−0.48	−7.3	−13.9	−6.3	−10.4
4	−7.4	−12.3	−21.2	−0.55	−0.15	−4.5	−29.9	−21.9	−24.9
5	−6.1	−10.7	−19.1	−0.86	−0.06	−3.9	−35.1	−26.6	−29.9
6	−7.5	−12.9	−22.2	−0.30	−0.30	−5.0	−28.5	−20.8	−25.3
7	−19.9	−19.8	−28.8	−0.59	−0.39	−4.9	−8.39	−0.5	−3.79

[a]Base 10 logarithm
[b]Sample identification: 1–Battle Mountain, 2–Gund Ranch, 3–Salmon Creek, 4–Fallon, 5–Red Rock, 6–Minden, 7–Spanish Springs

Activity of Fe(II) is controlled by $FeCO_3$ (siderite) at pe + pH ≤ 8 and by $Fe_3(OH)_8$ (ferrosic hydroxide) at pe + pH ≥ 8. In systems below pH = 6.0 with stable redox, less-soluble iron oxides such as geothite (alpha-FeOOH) can control Fe solubility (Schwab and Lindsay 1983). Levels of Fe(II) are presented in Table 3. Ferrous iron levels had a significant effect on the amount of Se extracted from soils (r = .5843). Siderite would control Fe(II) activity in the Spanish Springs and Clover Valley samples. Ferrous iron activity in the remaining samples would be controlled by ferrosic hydroxide. Hematite would control ferric iron activity of sample soils except for Spanish Springs and Clover Valley where ferroselite would control ferric iron (Fe III). Any remaining Fe(III) could be associated with hydrous selenite complexes.

Total Fe levels ranged from 8700 to 28000 mg/kg. Total Se and total Fe were not correlated for these soils (r = −.1028). Redox potential and total Fe had an effect on soil Fe(II) and Fe_2O_3 content (r = .4565 and r = .3998, respectively). A decrease in selenite adsorbed on iron oxide would depend on the adsorption density of selenite (moles of ion adsorbed/kg of oxide; Balistrieri and Chao 1987). Other ions in a soil solution, including P, can compete with selenite for adsorption sites on solid surfaces. Anion adsorption relies on several factors including pH, formation of solution complexes, and competing adsorbates (Mikkelsen et al. 1989). Phosphate displaced all the adsorbed selenite on allophane clays (Rajan and Watkinson 1976) and has been shown to desorb selenate (Singh et al. 1981).

Most P found in alkaline soil exists as calcium phosphate ($CaHPO_4$; Lindsay and Moreno 1960, Boyle and Lindsay 1986). Phosphate levels of study soils ranged from 8.9 to 147 mg/kg P. To evaluate the effect of P on selenite adsorption, we calculated total anion concentration ratios {(anion)/(selenite)}. Results are presented in Table 4. A stronger affinity and larger concentration of one anion should result in more sites being occupied by that anion vs. another (Balistrieri and Chao 1990). Levels of P, and Fe_2O_3 and P did not have an effect on the amount of Se extracted from the study soils (r = .3030 and r = .1019, respectively). Absence of a significant correlation between levels of Fe_2O_3 and P and extractable Se suggests that Se would exist in solution for these soils. Phosphorus would have displaced Se from available binding sites. Selenium-phosphate interactions are generally not of consequence for plant uptake of Se except for plants growing where levels of Se are inadequate to meet animal nutritional needs (Mikkelsen et al. 1989).

Mean concentration of total Se in soils and surficial materials for the western United States is 0.23 mg/kg, with an observed range of <0.10–4.3 mg/kg Se. Most soils from low-Se areas in the United States contain <0.5 mg/kg Se (National Research Council 1983, Boon 1989). A limited survey of Nevada soils, as part of a trace-element survey of soils throughout the United States, revealed a variety of Se levels (Shacklette et al. 1974). Observations in the Fallon area demonstrate that seleniferous spots may be found in alluvial Pliocene deposits occurring over a large part of Nevada, particularly in the Carson and Humboldt sinks (Lakin and Byers 1948, Rowe et al. 1991). Total soil Se levels in this study ranged from <0.10 to 0.74 mg/kg. As with many other elements, total concentration of Se in soils shows little relationship to Se concentration in plants grown in those soils.

TABLE 3. Total iron, extractable iron oxides, and ferrous iron in soil samples.

Sample location	Milligrams/kilogram[a]		
	Total Fe	Oxide Fe	Ferrous Fe
Battle Mountain	17000	4575	3290
Gund Ranch	28000	12175	6090
Spanish Springs	19000	8900	7920
Reno	27000	6550	5800
Minden	19000	3950	10940
Fallon	12000	3700	3010
Salmon Creek	12000	2525	8580
Clover Valley	8700	875	7060
Huntington Valley	19000	4350	5300
Red Rock	17000	6350	3220

[a]Air-dried basis

TABLE 4. Extractable phosphate phosphorus, selenite selenium, and phosphate/selenite molar ratios.

Sample location	Phosphate (10E-5 M)	Selenite (10E-7 M)	{(Phosphate)/ (selenite)}
Battle Mountain	3.4	1.3	271
Gund Ranch	3.5	2.5	136
Spanish Springs	15.2	28.9	52
Reno	23.9	0	0
Minden	1.4	29.1	5
Fallon	3.4	1.3	269
Salmon Creek	4.3	5.0	85
Clover	5.8	0	0
Huntington	4.6	0	0
Red Rock	4.1	2.5	160

Workmann and Soltanpour (1980) have reported that water-soluble Se is usually <50 μg/kg in normal cultivated soils. Soils in this study had soluble Se levels of <1–102 μg/kg, existing primarily as selenite. The significant correlation between pe + pH and levels of extractable Se ($r = -.4475$) suggests a relationship between the amount of Se available for plant uptake and soil redox potential at the study sites.

Certain native plants of the Great Basin have tendencies to aggregate in relation to temperature gradients, precipitation patterns, physiography, and soils (Tueller 1975, Reveal 1979). Approximately 80% of all forage and grain sampled in western Nevada has been shown to contain <0.10 ppm Se, less than the dietary requirement of 0.10 ppm for grazing animals (Kubota et al. 1967, McDowell et al. 1983, National Research Council 1983). Soil Se concentration can vary widely over a very short geographic distance (Fisher and Munshower 1991). Upper rangeland forage of extreme northeastern Nevada growing on Idavada volcanics and silicic rocks of volcanic origin was found to contain low levels of Se (Carter et al. 1969). In contrast, lower rangelands surrounding a portion of these areas produce forage adequate in Se (Carter et al. 1968). Alfalfa samples taken from the Carson Valley area were found to be below (<0.05 ppm) the dietary requirement of 0.1 ppm Se (Allaway and Hodgson 1964). Forage at Gund Ranch has been shown to contain 0.13–0.17 ppm Se (Poole et al. 1989). Selenium indicator plants are limited to localized areas on seleniferous geological formations in Nevada (Poole et al. 1989) and are not reported to occur within sample site areas.

Forage at the Fallon site would not be expected to contain appreciable amounts of Se. Soil redox potential does not allow for formation of plant-available selenate. In areas adjoining Carson Valley, including Fallon, white muscle disease in sheep has been a recognized problem (Vawter and Records 1947, Kuttler and Marble 1958) for animals raised on native forage. Soil at the Gund Ranch site supports a small fraction of selenate, allowing for growth of forage marginally deficient in Se. Grazing cattle have been found to be borderline deficient in plasma Se at the Gund Ranch site (Poole et al. 1986). Upper rangeland forage in the Salmon Creek area would be deficient in Se because of lack of available soil selenate. Samples lacking measurable amounts of extractable Se would not support growth of Se-bearing forage.

CONCLUSION

Total and extractable Se, redox potential, pH, and P, Fe(II), and Fe_2O_3 levels were different for each of the sample sites. Redox potential and Fe(II) and free Fe_2O_3 levels would affect the quantity of Se available for plant uptake in study soils. Anion concentration ratios indicate that P would influence adsorption of selenite on iron oxide. Soils in this study support selenite species that are not readily available to plants and therefore could not support vegetation adequate in Se.

Soil Se concentration can vary widely over a very short geographic distance. Nevada's complex geology therefore requires evaluation of the Se status of soils and vegetation on a site basis. Further studies are needed to develop a better understanding of the Se status of the state.

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